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I. INTRODUCTION

In this report, we describe the electrochemical polymerization reactions of aromatic compounds. The reactions described here are of the type first reported with the oxidation of pyrrole to produce polypyrrole [1,2]. There are several interesting facets of these reactions. First, the reactions have electrochemical stoichiometry and in this regard are different from the more traditional electrochemical polymerization reactions which are electrochemically initiated either directly or indirectly [3] and in which the bulk of the polymerization reaction takes place away from the electrode surface. Secondly, the product of the reaction is a film which is localized on the electrode surface, is electroactive, and has electrical conductivity [4-6]. In this regard, the reaction again distinguishes itself from the more common observations in organic electrosynthesis where the electrode is filmed with an insulating by-product which passivates the electrode [7].

The materials prepared by this method have the greatest attention in the area of conducting polymers [8]. This results from the fact that the films can be prepared from commercially available reagents in a relatively straightforward synthetic procedure. In addition, many of the thick free-standing films are stable in air and show little change in their electrical and mechanical properties when handled in air. These materials have also attracted the attention of the electrochemical community. Their interest ties in the electroactive properties and the electrode applications of these materials [9]. We now present a review of the electrochemical synthesis of the conducting thin films along with some of their interesting electrochemical properties. Also included in this review is a brief section which describes the chemical routes to the polymers of the pyrrole and the thiophene derivatives. This section is not intended to be an exhaustive presentation of all the synthetic work in the area of conducting polymers; instead we describe only those materials which are complementary to the electrochemically prepared polymers.

II. HISTORICAL BACKGROUND

The electrochemical preparation of conducting polymers dates back to early attempts of Dall'Olio and co-workers [1], who obtained "pyrrole black," as it was called at that time, on electrochemical oxidation of pyrrole in aqueous sulfuric acid as a powdery, insoluble precipitate on a platinum electrode. Elemental analysis showed that the pyrrole black so obtained consisted of 76% "polypyrrole," the remainder being sulfate ions; therefore the polymer was cationic. It was found to have an electrical conductivity of $\sigma = 8$ Ω^{-1} cm^{-1}, and gave rise to an intense electron spin resonance signal with a g value of 2.0026, indicating the abundance of free spins.

Electrochemical Synthesis

But it was not until subsequent experiments [2] in 1979 that the importance of the electrochemical approach to the synthesis of conducting polymers became apparent. The key difference between these later and the earlier experiments was that now continuous films were obtained which could be peeled off the platinum electrodes to yield free-standing, easily manageable films that were stable in air and had much higher electrical conductivities than achieved before, namely, $\sigma = 100$ Ω^{-1} cm^{-1}. The availability of free-standing films provided access to a variety of electrical and modern analytical tests, which the well-known chemical oxidation products of pyrrole [10], namely, the amorphous, insoluble "pyrrole black" powders, had not permitted.

With regard to their structure, it was believed that the pyrrole blacks consisted of pyrrole units with preserved aromatic character, coupled chiefly via their 2- and 5-positions. This conclusion was based on two pieces of information. First, the oxidation degradation of the "pyrrole blacks" powder yielded pyrroledicarboxylic acid with the carboxylic groups in the 2- and 5-positions, plus a small fraction of pyrrole derivative with an additional carboxylic group in the 3-position [10]. Even the low molecular weight by-products which are soluble in the reaction mixture are 2,5-coupled. Secondly, 2,5-disubstituted pyrroles do not polymerize. Monosubstituted pyrroles with the substituent in the 2-position produced soluble dimeric products instead of polymer films [11].

III. GENERAL CONSIDERATIONS

A. Aromatic Monomer

All the compounds which have successfully produced conducting films have several basic characteristics. First, they are aromatic and can be oxidized at relatively low anodic potentials. This removes complications arising from the oxidative decomposition of the solvent and electrolyte. As can be seen by the values listed in Table 1, the aromatic monomers which electropolymerize

TABLE 1 Electrochemical Data for Some Aromatic Compounds

Compound	Peak potential	n	References
Pyrrole	1.2	2.2-2.4	5
Bipyrrole	0.55	–	18
Terpyrrole	0.26	–	18
Thiophene	2.07	2.08	6,18
Bithiophene	1.31	2.22	6,18
Terthiophene	1.05	–	18
Azulene	0.91	2.2	6
Pyrene	1.23	2.31	6
Carbazole	1.30	2.45	6

have peak potentials below 2.1 V. Second, the aromatic compound undergoes electrophilic substitution reactions where the aromatic structure is maintained. Although the polymerization reactions being described here proceed via radical coupling (as will be discussed below), the susceptibility of a given compound toward electrophilic substitution is a fair guide in determining whether it will electropolymerize in the form that is being discussed here.

In addition, the stability of the incipient cation is also an important although more subtle consideration for the formation of polymer film. Film formation results from cation intermediates with intermediate stability which favor the radical coupling reaction. The more stable cations diffuse away from the electrode surface and produce soluble products. The very reactive cations will react indiscriminately with solvent and other nucleophiles in the region of the electrode surface, minimizing the polymer-forming reaction.

B. Electrolytic Conditions

Recognizing that the polymerization reaction proceeds via radical cation intermediates, it becomes apparent that the reaction will be sensitive to the nucleophilicity of the environment in the region near the electrode surface. This then places some limitations of the choice of the solvent and the electrolyte. For this reason, many of the reported studies have been performed in aprotic solvents, which are poor nucleophiles. Among these, acetonitrile has been the most commonly used solvent, although a wide variety of other aprotic solvents can be used as long as the nucleophilic character of the solvent is poor. However, certain nucleophilic aprotic solvents, such as dimethylformamide, and hydroxylic solvents can also be used to prepare good films if the nucleophilicity of the solution is reduced using protic acids. This topic is discussed in more detail in the section involving polypyrrole.

With regards to the electrolyte salt, the main considerations are the solubility, degree of dissociation, and the nucleophilicity. For this reason, most of the salts used are tetraalkylammonium salts, since they are soluble in aprotic solvents and are highly dissociated. Although some lithium salts are soluble in aprotic solvents. In general, these salts are highly aggregated. Most sodium and potassium salts are poorly soluble in aprotic solvents. A wide variety of anions can be used as tetraalkylammonium salts, as is discussed below. Good films are typically not produced when the anion is a halide, because halides are fairly nucleophilic and easily oxidized. The highly nucleophilic anions, such as hydroxide, alkoxide, cyanide, acetate, and benzoate, do not produce good-quality films either and instead produce soluble products which color the reaction solution [12]. This is not surprising, since the cyanide anion is known to react efficiently with the electrochemically generated cation of pyrrole [13].
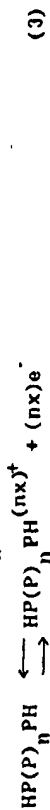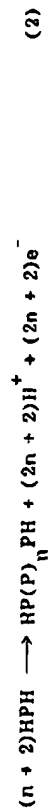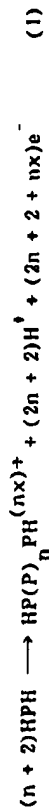
C. Electrodes

The best films have been prepared in a divided cell using three electrodes where the counterelectrode is seperated from the working and the reference electrode. The nature of the working electrode is a critical consideration for the preparation of these films. Since the films are produced by an oxidative process, it is important that the electrode does not oxidize concurrently with

the aromatic monomer. For this reason, most of the available films have been prepared using a platinum or a gold electrode. However, as we have reviewed in more detail [9], films have been prepared using a variety of semiconducting materials, including tin oxide, n-type polycrystalline silicon [14], gallium arsenide [15], cadmium sulfide and cadmium selenide [16], and graphite [17].

In the majority of the cases, the films are produced so readily that the only serious limitations are the nucleophilic nature of the solution and the nature of the working electrode. In fact, as in the case of polypyrrole, films can be produced using a simple two-electrode, undivided cell which is powered by a DC battery. However, films prepared in this manner are of poorer quality because of the complications that this cell configuration presents.

IV. STOICHIOMETRIC POLYMERIZATION REACTION

One very important aspect of this reaction is that it has electrochemical stoichiometry. In this regard, the reaction resembles the electrodeposition reactions of metals more than the electropolymerization reactions which by and large are electroinitiated reactions. The apparent stoichiometry for the film-forming reaction is in the range 2.06-2.5 Faraday/mol of monomer, as can be seen in Table 1. This stoichiometry is formalized in Eq. (1), where HPH represents an aromatic ring with hydrogens on the two active carbon centers:

$$(n + 2)HPH \longrightarrow HP(P)_n PH^{(nx)+} + (2n + 2)H^+ + (2n + nx)e^- \qquad (1)$$

$$(n + 2)HPH \longrightarrow HP(P)_n PH + (2n + 2)H^+ + (2n + 2)e^- \qquad (2)$$

$$HP(P)_n PH \rightleftharpoons HP(P)_n PH^{(nx)+} + (nx)e^- \qquad (3)$$

The apparent stoichiometry for the polymerization reaction includes the stoichiometry for the formation of the polymer chain, which is 2.0 for large values of n (eq. (2)), plus the charge associated with the oxidation of the polymer [Eq. (3)]. Although the degree of polymerization is not known for these polymers, estimates suggest that it could be as low as 10 or as high as 1000 aromatic rings per chain [18,25b]. Each polymer has a different stoichiometry where the variation results from the degree of oxidation of the polymer. This characteristic of the reaction is very useful, since it provides some control on the amount of film that is produced. This control is only practical when the monomer has a relatively low oxidation potential and there are no interfering side reactions which consume charge.

V. MECHANISTIC CONSIDERATIONS

The polymer chains consist of linked aromatic units, which in the case of pyrrole and thiophene are primarily 2,5-coupled, while in the case of azulene the coupling is via the 1- and 3-positions. For all these compounds, the coupling occurs at the carbon atoms, which are known to be the most reactive toward addition and substitution reactions. The polymerization reaction is a very complicated one, where the general reaction steps are as shown in Scheme 1.

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ent on time and independent of the concentration of pyrrole for a constant potential electrolysis [19,20]. Under the steady-state conditions, the coupling reaction must also occur between the radical cations of pyrrole and the radical cations of the oligomers, since the dimer, trimer, and polymer are more easily oxidized than the monomer [18]. Therefore they will also be present in the oxidized state and not the neutral form during the polymerization reaction. Under steady-state conditions, the current depends on the rate of diffusion of pyrrole to the region of the electrode [19]. With regards to the subsequent aromatization reaction, the sequence of the various steps is not known.

VI. DERIVATIVES OF PYRROLE

A. Effect of Solvent

As was briefly mentioned above, the solvent has a very strong influence on the outcome of the electro-oxidation reaction. As can be seen in Table 2 for the electrochemical reactions of pyrrole, a wide variety of aprotic solvents can be used, as long as the nucleophilic character of the solvent is poor [12]. (In this discussion of the data in Table 2, a good film is one that is removed intact from the electrode and which is not fragile or powdery.) If the nucleophilic character of the solvent is enhanced, film formation is minimized. This can be seen from the result of adding a small amount of pyridine to the acetonitrile solution. Films are not produced in the nucleophilic aprotic solvents such as dimethylformamide, dimethylsulfoxide, and hexamethylphosphoramide, unless the nucleophilicity of the solution is reduced by the addition of the protic acid. Hydroxylic solvents can also be used. As we mentioned above, the first electropolymerization of pyrrole was performed in aqueous media. The films so obtained are of poorer quality. They are brittle and powdery, with little physical strength, and have lower conductivity values. In solvents with nucleophilic characteristics intermediate between water and the aprotic solvents, such as alcohol and mixed aqueous-aprotic solvent mixtures, films can be prepared with intermediate conductivity values and good physical strengths. The quality of these films can be improved by adding a protic acid to the reaction solution in order to reduce its nucleophilic character.

Even when considering only those solvents which permit the formation of good films, the mechanical and electrical properties of the resulting films can be varied by changing the solvent. The importance of the solvent was demonstrated with the polypyrrole toluenesulfonate films. Thick films which could be removed from the electrode were prepared in aqueous acetonitrile solvent mixtures. The conductivity of these films could be made to change from 100 to $0.5 \ \Omega^{-1} \ cm^{-1}$ by increasing the water content from 1 to 33% [21]. With higher concentrations of water, the conductivity increased slowly up to $50 \ \Omega^{-1}$ cm^{-1}. These results are shown in Figure 1. There is a corresponding change in the mechanical properties of the films. The films are continuous and are generally strong and hard. They have tensile strengths which are in the range 1200-8600 psi, and Young's modulus values in the range 70,000-350,000 psi. Films which are prepared in acetonitrile containing 1% water are about seven times stronger than the films prepared in 25% water-75% acetonitrile. The dry films are not stretchable and break at small elongations (4-8%). These results are listed in Table 3. The conductivity and the strength of the films are also reduced when ethylene glycol is used as a cosolvent, although the influence of ethylene glycol is milder than water [21].

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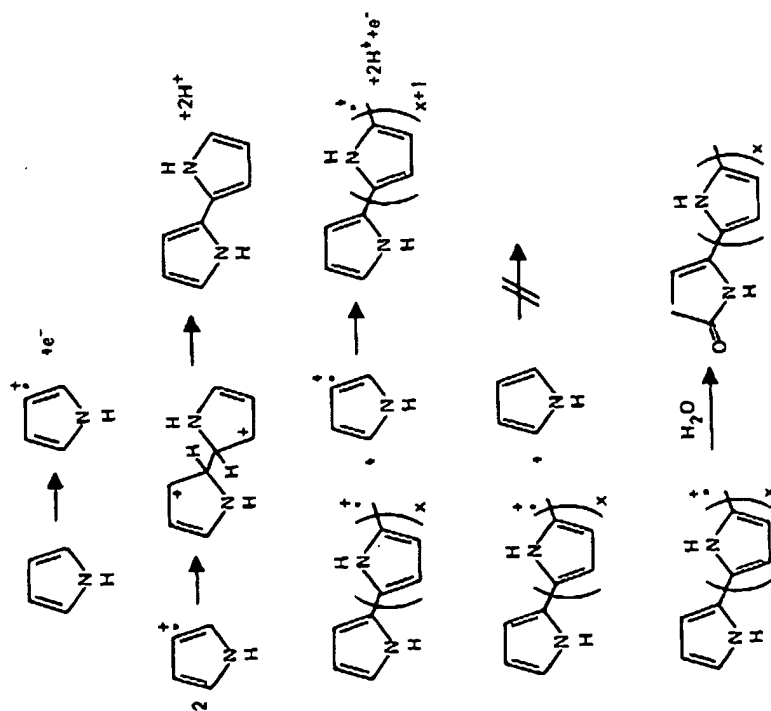
SCHEME 1 Electropolymerization of pyrrole. (From Ref. 19.)

After the initial oxidation step, there is a coupling reaction, followed by a deprotonation and a one-electron oxidation in order to regenerate the aromatic system. From a mechanistic point of view, there are two unique stages to the coupling reaction. There is the initial coupling reaction, which involves the coupling of pyrrole monomers to produce the dimeric intermediates, and there is the steady-state coupling reaction, which involves the reaction between the pyrrole monomer and the oligomeric and polymeric intermediates. Considering the coupling reaction in the initial stages of the reaction, the originally formed radical cation could undergo a radical coupling reaction with another radical to form a dimer, or it could react like an electrophile and add to a neutral monomer. Since the polymerization reaction proceeds only when the potential is sufficiently high to oxidize the monomer, the coupling reaction must involve the coupling of two radical cations. At these potentials, the concentration of the neutral aromatic species is zero at the electrode and negligible in the region of the electrode. In the initial stages of the reaction, the charge consumption which accompanies the rate of polymer formation is linearly depend-

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TABLE 2 Solvent Effects of the Quality of the Generated Polypyrrole Films

Solvent/electrolyte (0.1 M)[a]	Film quality	Conductivity (Ω^{-1} cm^{-1})
Acetonitrile/tetraethylammonium tetrafluoroborate	Good film	50
Acetonitrile/toluenesulfonic acid	Good film	50
Acetonitrile/tetraethylammonium tetrafluoroborate plus 1.0 M pyridine	No film	—
Methylene chloride/tetrabutyl-ammonium tetrafluoroborate	Good film	50
Butanone/tetrabutylammonium tetrafluoroborate	Good film	40
Propylene carbonate/tetrabutyl-ammonium tetrafluoroborate	Good film	50
Dimethylformamide/tetraethyl-ammonium tetrafluoroborate	No film	—
Dimethylformamide/toluenesulfonic acid	Good film	20
Dimethylsulfoxide/tetraethyl-ammonium tetrafluoroborate	No film	—
Hexamethylphosphoramide/tetra-ethylammonium tetrafluoroborate	No film	—
Ethanol/tetrabutylammonium tetrafluoroborate	Rough, flaky	0.2
Ethanol/toluenesulfonic acid	Good film	3
Ethanol/sulfuric acid	Good film	3
Ethanol/phosphoric acid	No film	—
Ethanol/hydrochloric acid	Thin, very low yield	—

[a] Pyrrole (0.01 M) was oxidized on a platinum electrode.
Source: Ref. 12.
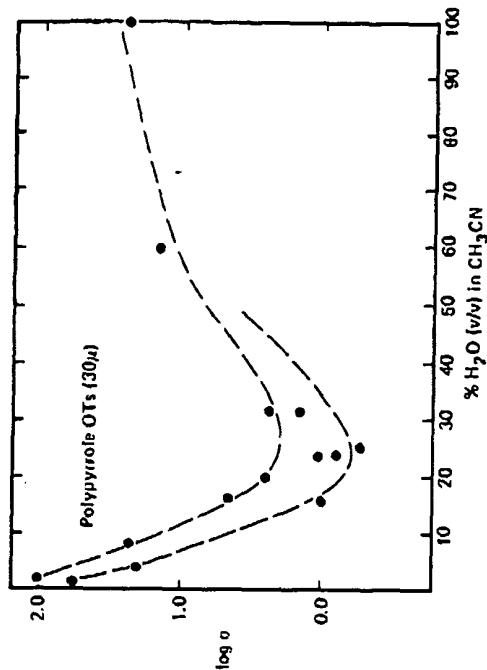

Polypyrrole OTs (30μ)

% H$_2$O (w/v) in CH$_3$CN

log σ

FIGURE 1 Plot of log σ for polypyrrole toluenesulfonate films versus percent water in the film preparation solution. (From Ref. 21.)

TABLE 3 Polypyrrole Toluenesulfonate Films Prepared in Acetonitrile

Cosolvent	Conductivity (Ω^{-1} cm^{-1})	Tensile strength (psi)	Elongation at break (%)
1% water	60-100	8600	4
25% water	0.5	1200	4
25% ethylene glycol	25	4750	5
50% ethylene glycol	29	7210	8
1% water-1% ethylene glycol	40	7350	8
5% water-5% ethylene glycol	4-17	5900	14
25% water-25% ethylene glycol	13	5310	6
50% water-50% ethylene glycol	17	2700	6

Source: Ref. 21.

The origin of the variation in the properties of these films is not known. There is no observable difference in the degree of oxidation of the polymer, the composition, or the general appearance of the film. Films prepared in acetonitrile containing 1% water and 12.5% water ethylene glycol have the same elemental composition, and this corresponds to having 0.28-0.32 toluenesulfonate anions for every pyrrole unit. The flotation density of the film also remains unchanged at 1.36 g/cm³. The variation in the conducting and mechanical properties of the films may result from a variation in the chain lengths of the polymer, where shorter chains are produced in the presence of water and ethylene glycol. The chains are still quite long, since all the polymer films are totally insoluble.

B. Counteranion

When in the conducting form, the electropolymerized films contain 10-35% anion (by weight) which is affiliated with the cationically charged polymer chains. The amount of anion found in each film is governed by the level of oxidation of the polymer and is a characteristic of each film. The anion contents for the various films are listed in Table 4. This polymer-anion compositional balance of the films actually proves to be quite useful, since the properties of the films can be conveniently altered by changing the anion. Since the anion in the film is incorporated from the electrolyte salt in the preparative solution, the modifications can be made by simply changing the electrolyte salt of the solution.

In the case of the polypyrrole films, a wide variety of anions have been used to prepare thick free-standing films [22], and can be seen in Table 5. The anions listed in Table 5 are poorly nucleophilic and permit the formation of good-quality films. Tetraalkylammonium salts were used in the preparation of these films. These films are hydroscopic and will lose 5-7% moisture when dried at 110°C. The level of oxidation of polypyrrole is 0.25-0.32 per pyrrole

TABLE 4   Anion Content of Conducting Films

Film	Oxidation level	Anion content (% by wt)	References
Polypyrrole	0.25-0.33	25-30	5
Polythiophene	0.06	7-25	31,32
Polybithiophene	0.22	12	31
Azulene	0.25	15-28	32,51
Pyrene	0.45	–	–
Carbazole	0.45	21	6
Indole	0.2-0.3	15-20	51
Furan	–	26	32

TABLE – Polypyrrole Films with Different Anions

Anion	Oxidation level	Density (g/cm³)	$\sigma(\Omega^{-1}\,cm^{-1})$
Tetrafluoroborate	0.25-0.32	1.48	30-100
Hexafluoroarsenate	0.25-0.32	1.48	30-100
Hexafluorophosphate	0.25-0.32	1.48	30-100
Perchlorate	0.30	1.51	60-200
Hydrogen sulfate	0.30	1.58	0.3
Fluorosulfonate	–	1.47	0.01
Trifluoromethylsulfonate	0.31	1.48	0.3-1
p-Bromobenzenesulfonate	0.33	1.58	50
p-Toluenesulfonate	0.32	1.37	20-100
Trifluoroacetate	0.25	1.45	12

Source: Ref. 22.

unit, corresponding to one anion for every 3-4 units. The level of oxidation is an intrinsic characteristic of the polymer and is not sensitive to the nature of the anion. The anion, however does influence both the structural properties and the electroactivities of the films. As can be seen in Figure 2, the topology of the surface is dramatically different for films containing the various perfluoride, sulfonate, and carboxylate anions (22). The differences observed between the surfaces is not reflected in the packing structure of the bulk material. Thus, with the exception of one or two of the anions listed in Table 5, all of the films have similar flotation densities which are in the range 1.45-1.51 g/cm³.

Likewise, the mechanical properties of the films change with the anion. Polypyrrole films containing toluenesulfonate, perchlorate, and fluoroborate anions are hard and strong films and stretch very little (4-5% elongation at break). However, the films containing toluenesulfonate anion are stronger and have tensile strength values which are about 30-40% higher than for the other films. The conductivities, elongation, and moduli values are similar for these films.

Films with electroactive anions have also been prepared. For example, polypyrrole films with ferricyanide anion were prepared using the tetraalkyl-ammonium salt of the anion in acetonitrile solution [23]. The iron phthalocyanine tetrasulfonate anion was also incorporated into a polypyrrole film by preparing the film in aqueous solutions [17].

The anions have a strong influence on the electronductivity and the conductivity of the films. This effect is discussed in the following section.
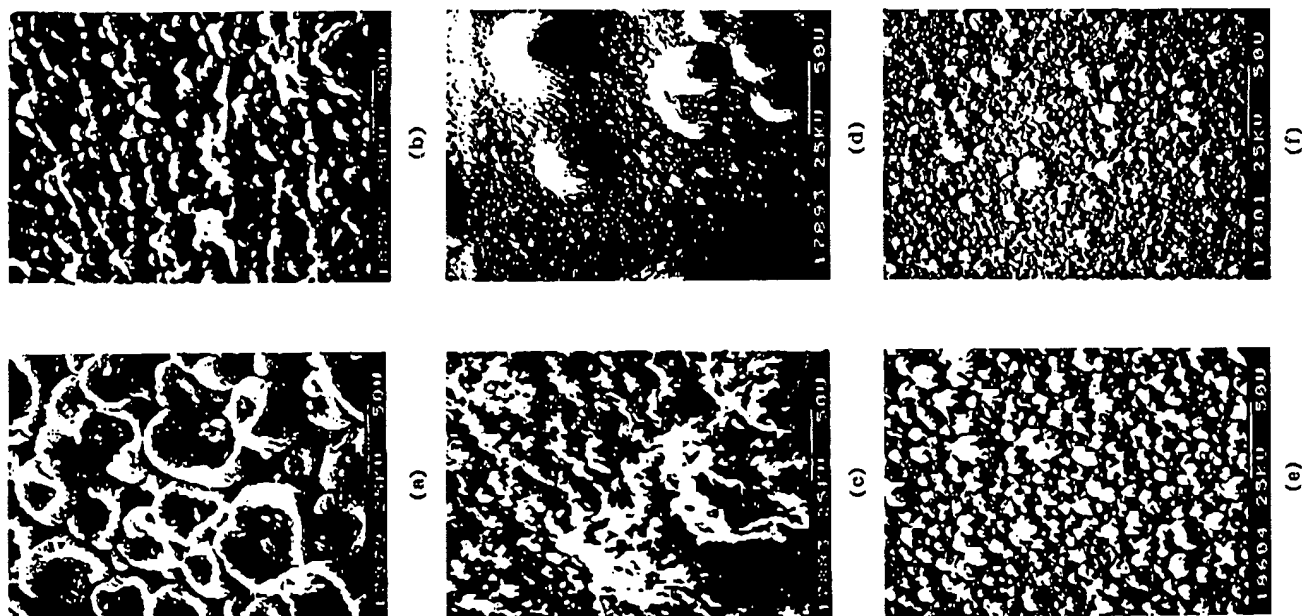
C. Substituents

The properties of the films can also be modified by polymerizing pyrrole derivatives with substituents in the nitrogen (24) and the 3-position [6, 22, 25]. In this way films have been prepared with alkyl and aryl substituents in the nitrogen and the 3-positions of the pyrrole unit. Judging from the methyl substituent, the properties of the films are more sensitive to the presence of a substituent on the nitrogen than in the 3-position. The film produced from the polymerization of N-methylpyrrole resembles the polypyrrole films in many respects. It is a continuous film which has the physical appearance of polypyrrole. It consists of about 80% poly-N-methylpyrrole and about 20% tetrafluoroborate anion. This corresponds to approximately 1 anion for every 3-4 pyrrole units. The flotation density of the film is 1.46 g/cm^3 which is close to the value for the polypyrrole film. These results are summarized in Table 6. The temperature stability is also similar to that of the polypyrrole films. Both materials show a gradual weight loss with heating up to 250–300°C and a more rapid weight loss at the higher temperatures. β-Methyl-substituted pyrrole derivatives also polymerize to produce films on the electrode surface. In this way, continuous films have been prepared by polymerizing 3-methylpyrrole [6] and 3,4-dimethylpyrrole [25] in acetonitrile solutions containing tetraethylammonium tetrafluoroborate. The degree of oxidation of the polymer chain remains at about 0.25 charges per ring and is not affected by the methyl group, and the density of the film is reduced to 1.36 g/cm^3. The big difference between the polypyrrole and the polymethylpyrrole films is in the active properties where the introduction of the methyl group reduces the conductivity and shifts the oxidation potential of the films. These characteristics are discussed below.

TABLE 6 Some Data for Alkyl-Substituted Polypyrrole Tetrafluoroborate Films

Alkyl group	Thin films ($E°/mV$)	Oxidation level	Density (g/cm^3)	Thick films σ (Ω^{-1} cm^{-1})
–	–200	0.25–0.30	1.48	30–100
N-Methyl	450	0.23–0.29	1.46	0.001
3-Methyl	–240	0.25	1.36	4
3,4-Dimethyl	–100	–	–	10
N-Ethyl	450	0.20	1.36	0.002
N-Propyl	500	0.20	1.28	0.001
N-n-Butyl	640	0.11	1.24	0.0001
N-i-Butyl	600	0.08	1.25	0.00002

Source: Refs. 5 and 6.

FIGURE 2 Scanning electron micrographs of polypyrrole film surfaces. The anion in the film is (a) hexafluorophosphate, (b) perchlorate, (c) sulfate, (d) trifluoromethylsulfate, (e) fluorosulfonate, and (f) trifluoroacetate. (From Ref. 22.)

Polymer films can also be prepared with ethyl, propyl, and butyl groups on the nitrogen position; however, the quality of the film with the latter groups is very poor [24]. The quality and yield of the films become quite poor when the N-alkyl group is butyl or bigger. The films prepared from pyrrole containing an n-butyl or an i-butyl group are not smooth instead, they are rough and wrinkled. The yield of film is low and is accompanied by the formation of soluble products which darken the solution. These films are less oxidized than polypyrrole and have 0.08-0.11 charges per aromatic unit. They are also less conducting. With the presence of a t-butyl or a cyclohexyl substituent, continuous films are not produced. The deposit formed on the electrode is a brown-black powder. From these results, it is clear that steric effects alone are an important factor in the preparation of continuous films with a reasonably high conductivity. The differences observed here are not due to electronic effects, since the inductive effects of these substituents and of the hydrogen atom are very similar. For example, the oxidation peak potentials for all of these derivatives are close and in the range of 1.2-1.4 V. The results may be due to steric effects alone. Steric effects must be important both in the coupling step of the polymerization process and in the determination of the degree of coplanarity of the aromatic rings along the polymer chain. The latter will influence the conductivity of the films.

A series of poly-N-arylpyrrole films have also been prepared. These films are generally more difficult to prepare and must result from both the steric and electronic effects of the aryl group. The inductive effects of the aryl group makes these monomers much more difficult to oxidize. The oxidation peaks for these derivatives are in the range 1.3-1.8 V versus SSCE (Table 7). The higher potentials required to oxidize these derivatives permits side reactions to compete with the film-forming reaction. Poly-N-phenylpyrrole tetrafluoroborate films can be grown 25-40 μm thick and be removed from the electrode surface. The films are visually similar to the polypyrrole films. They are less oxidized, where there is 0.15 charge per pyrrole unit, and are correspondingly less conducting. The films have densities like polypyrrole. Thin films have also been prepared from phenylpyrrole derivatives with nitro, methyl, and methoxy substituents in the para positions of the phenyl group [26]. These films were prepared in thin form and their electrochemical prop-

erties were studied. The preparation of these films appears to be a fairly clean process, since the solution is not colored by the formation of soluble side products. However, thicker films of this material are difficult to prepare. No information is available on the corresponding thicker free-standing films.

D. Electroactivity and Conductivity

Many of the electrochemically prepared polymer films are electroactive and can be switched between the neutral and nonconducting state to the oxidized and conducting state. This behavior was first demonstrated with thin polypyrrole films, 200-400Å thick [27,28]. In the case of the polypyrrole films, the oxidation reaction is chemically reversible and can be driven repeatedly without loss of electroactivity. Because of the low oxidation potential of this polymer, it is very sensitive to the oxygen in the air. Therefore switching experiments must be performed in the absence of oxygen. The switching reaction involves the oxidation of an organic structure to produce a delocalized cationic intermediate, and the limitations in the choice of solvent and electrolyte salt which exist for the preparation of the films are also an important consideration with this reaction. However, the switching reaction is much more tolerant to the nucleophilicity of the solution than is the electropolymerization which is probably due to the difference in the relative stabilities of the cations involved in the two reactions. The majority of the electrochemical studies have been performed in acetonitrile. [29]; however, aqueous solvents have also been used.

The rate of switching is limited by the mobility of the anion in and out of the film where the linear diffusion rates are 10^{-10} cm^2/sec [19]. As a result, the switching rates are very sensitive to the anion (Fig. 3), and, in general, the rate of oxidation is slightly faster than the rate of reduction. This rate dependency on the anion gives rise to very complicated cyclic voltammograms which represent the combined faradaic and capacitive currents [30], and whose forms are not fully understood. The anion only influences the kinetics of the reaction and does not influence the switching potential.

The switching potential of the films is sensitive to the presence of substituents along the polymer chain. This is probably the most important factor when considering the use of these films for real applications, since the value of the switching potential establishes the stability of the film in air. With the presence of any substituent on the nitrogen of the pyrrole unit, the switching potential of the film moves anodically by about 0.6 V, which is sufficient to make the film stable in air (Fig. 4). This added stability greatly simplifies the handling and storage procedures for these films.

The electroactive character of these films can be altered and additional electroactive centers incorporated. This has been accomplished by placing the nitrophenyl group on the nitrogen of the pyrrole ring [26]. The resulting polymer has two separate switching potentials which correspond to the reaction of the polypyrrole backbone and of the nitrophenyl groups. Alternatively, additional electroactive centers have been incorporated into the film by way of the anions. Films with the electroactive anions ferrocyanide [23] and iron phthalocyanine-tetrasulfonate [17] have been prepared. In both cases the films with the best electrochemical response were prepared by having the electroactive anion in the preparative solution, rather than by attempting an anion metathesis with the fully formed film.

TABLE 7 Some Data for Poly-N-Arylpyrrole Thin Films

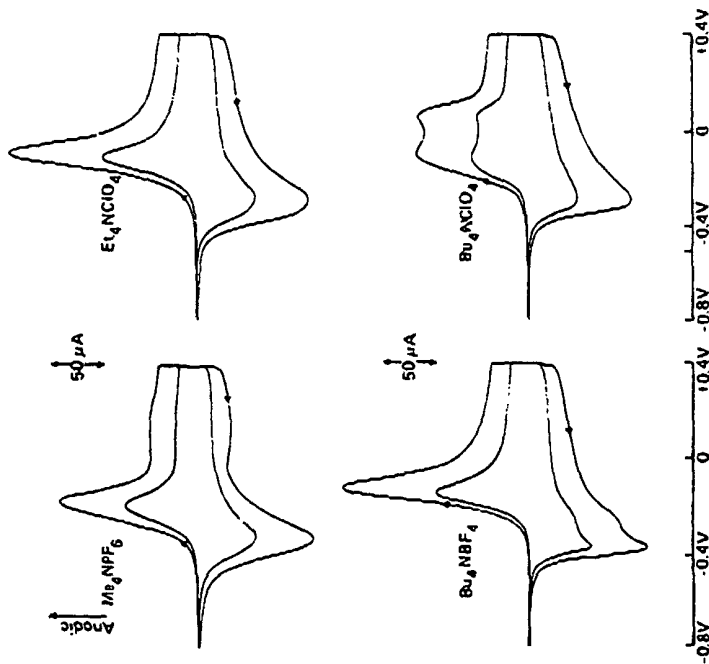| Monomer | | Polymer | |
p-N-Aryl	E_{pa}/mV	E_{pa}/mV	E_{pc}/mV
Methoxyphenyl	1360	700	600
Methylphenyl	1500	700	600
Phenyl	1800	740	600
Nitrophenyl	1600	920	780

Source: Ref. 26.

FIGURE 3 Cyclic voltammogram of a polypyrrole film (20 nm thick) on a platinum substrate immersed in acetonitrile solution containing various electrolyte salts (sweep rates: 50 and 100 mV/sec). (From Ref. 28.)

The anion also influences the electrical properties of the films which are in the oxidized form [22], where, in general, the films with the perfluoride and the perchlorate anions are more conducting (30-200 Ω^{-1} cm^{-1}) than the films with the sulfonate and carboxylate anions (0.01-10 Ω^{-1} cm^{-1}). The exception is the films containing the aromatic sulfonato anions (50 Ω^{-1} cm^{-1}), which are as conducting as the films with the perfluoride anions. The temperature sensitivity of the electrical properties of the films is also influenced by to the nature of the anion. Films with fluoroborate, fluorophosphate, perchlorate, nitrate, and toluenesulfonate anions which have room temperature conductivities of 50-100 Ω^{-1} cm^{-1} can be heated to approximately 160°C in air before they begin to decompose. Furthermore, the change in conductivity with temperature is very mild, 10-50% per 100°. Films with toluenesulfonate and trifluoroacetate anions which have room temperature conductivities of 4-12 Ω^{-1} cm^{-1} can be heated to 250-280°C before they begin to decompose. The conductivity of the latter films increase by a factor of 3-5 per 100° increase in temperature, where the less conducting film shows the biggest change.
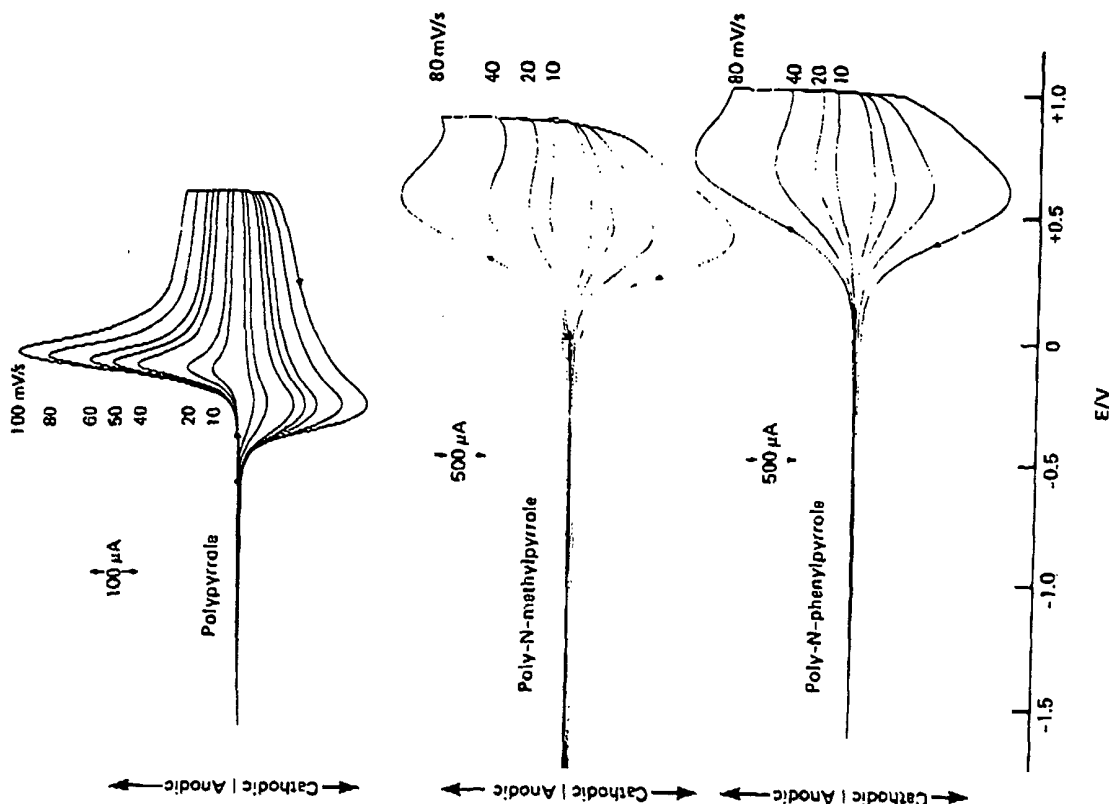
FIGURE 4 Cyclic voltammograms of polymer films of pyrrole derivatives measured in acetonitrile containing tetraethylammonium tetrafluoroborate. (From Refs. 4 and 5.)

VII. POLYTHIOPHENE

Thiophene provides a system closely related to pyrrole, and thus polypyrrole, but in a certain respect it is easier to study. For example, a wide variety of substituted thiophenes are commercially available, whereas 3-mono- or 3,4-disubstituted pyrroles are difficult to synthesize. However, not all thiophene monomers yield conducting amorphous polymer films (Table 8) [6]. Those which do represent a data set that allows to test a few concepts about the molecular framework of this polymeric form of heterocycles as well as about the bonding structure and conduction mechanism in polythiophenes [31].

All of the monomers show irreversible oxidation peaks and give rise to colored solutions upon electro-oxidation. The value of n for the oxidation reaction was estimated [6] from the Nicholson-Shain treatment for a totally irreversible electron transfer process which provides $n^{3/2}D^{1/2}$, where D was assumed equal to 10^{-5} cm²/sec. In general, the reaction of the compounds which produce polymer films occurs on the electrode surface and has n values between 2 and 3 as estimated from cyclic voltammetry [33]. From elemental analysis of some of these polymers, n values between 2.07 and 2.17 are obtained.

TABLE 8   Cyclic Voltammetric Data for Thiophenes Using Pt versus SSCE in 0.1 M TBAFB-CH₃CN with a Sweep Rate of 50 mV/sec

| Compound | Monomer | | | Polymer |
	E_{pa} (V)	$i/AC_v^{1/2}$ (A cm mol⁻¹ sec 1/2 V⁻¹/2)	n	E_{pa} (V)
Thiophene	2.06	3791	2.7	0.95
3-Methylthiophene	1.86	3202	2.4	0.72
3-Iodothiophene	2.03	2362	2.0	–
3-Bromothiophene	2.10	3085	2.3	1.06
3-Thiopheneacetonitrile	2.22	2725	2.2	1.12
3-Thiophenecarboxylic acid	2.28	1031	1.2	–
3-Cyanothiophene	2.46	2260	1.9	–
3-Nitrothiophene	2.69	2476	2.0	–
2,5-Dimethylthiophene	1.77	1134	1.2	1.33
3,4-Dibromothiophene	2.23	–	–	–
3-Thiophenemalonic acid	2.02	–	–	–
2-(3-Thienyl)pyridine	1.69	–	–	–
2,2'-Bithiophene	1.32	–	–	1.00

Source: Ref. 31.

The reaction of the compounds which produce soluble products, and therefore occur away from the electrode, has n values between 1 and 2, depending upon whether monomer (n=2) or dimeric (n=1) products are formed [11]. Accordingly, the α,α'-blocked 2,5-dimethylthiophene has an n value of 1.2, similar to that for 2,5-dimethylpyrrole [11].

The oxidation potentials of the monomers (Fig. 5) yield a linear correlation with the σ⁺ Hammet constants [34] for para substituents in the reaction type R⁰→R⁺. The shift in the peak oxidation potentials of the series of β-substituted thiophenes is dependent on three parameters, namely, their polar, steric, and mesomeric effects, which are exerted by the substituents [34]. This behavior can be described by the usual Hammett-Taft equation

$$R = \rho_n \sigma + S$$

where $\rho_\pi \sigma$ describes the polar-mesomeric parameters and S accounts for the steric factor [34b]. Accordingly, Figure 5 allows three conclusions to be drawn. First of all, the linear fit indicates that all of the monomers are oxidized by the same mechanism, that is, electro-oxidation results in the removal of a π electron from the thiophene ring. Secondly, the positive sign for ρ_π reveals that as the substituents take on more electrophilic character, the oxidation of the corresponding thiophenes proceeds less readily. Finally,
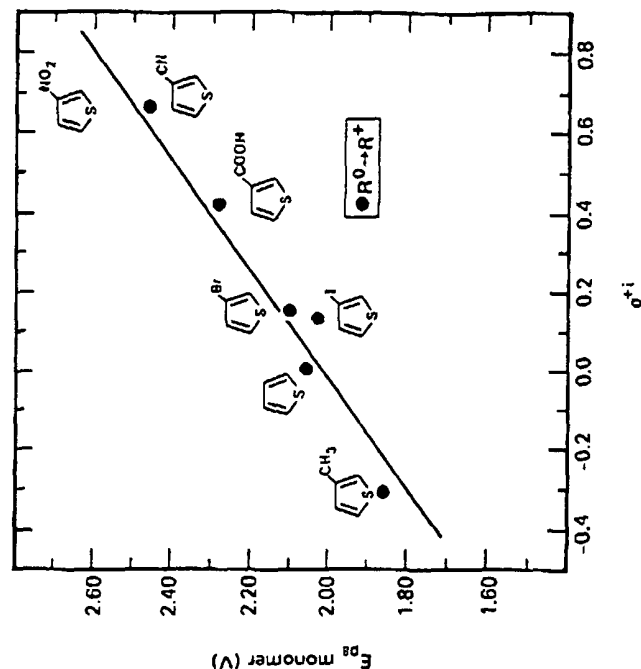

FIGURE 5   Electrochemical peak oxidation potential of thiophene monomers versus their respective Hammett substituent constants. (From Ref. 33.)
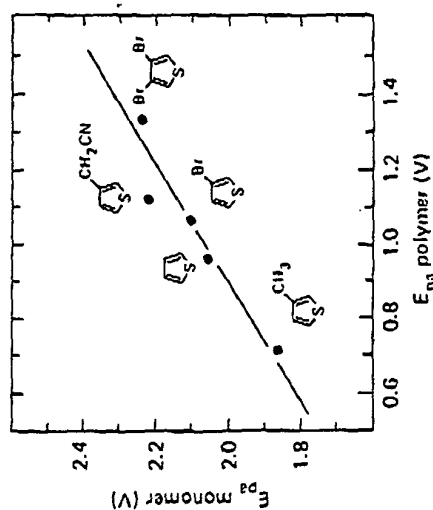
the steric term S appears to be minimal, since for the substituents chosen here a straight line is obtained. Thus the primary effect exerted by the β substituents is electronic and described by the $\rho_\Pi\sigma$ term.

Polymer films are produced only from the parent thiophene and the methyl-, bromo-, and iodo-substituted thiophenes. The latter two monomers yield poorly conducting films, while the other two polymers, polythiophene and poly(3-methylthiophene), have conductivities of about 10^{-2}-10^{-1} and 1 Ω^{-1} cm^{-1}, respectively. 3-Thiophene carboxylic acid, 3-cyano-, and 3-nitrothiophene yield no polymers on electro-oxidation under these conditions. These facts together with the above $\rho\sigma$ relationship (Fig. 5) suggests that there is an optimum potential range, that is, reactivity of the radical cation intermediate, which favors radical-cation coupling in the follow-up reaction to yield polymeric films [33]. Thus as the reactivity of the radical cation intermediate increases, the chemical selectivity is decreased and the intermediates may react indiscriminately with the solvent or other nucleophilic species in the vicinity of the Pt surface. Thus the presence of these strong electron-withdrawing groups may destabilize the radical cation intermediate to the extent that the radical-cation coupling reactions compete unfavorably with other reaction pathways.

While steric factors seem unimportant in the primary electro-oxidation of the monomer (Fig. 5), the follow-up coupling reactions are susceptible to steric effects. This may explain the overall inferior quality of the polymer films derived from the 3-bromo- and 3-iodothiophenes, even though their oxidation potentials do not differ greatly from that of the parent thiophene monomer. It is, however, interesting to note that while a bulky substituent such as iodo allows polymerization (albeit yields a film of poor quality), a sterically smaller cyano group does not.

The peak oxidation potentials for the substituted monomers are linearly correlated with the corresponding potential for the respective polymers (Fig. 6). The straight line fit suggests that β-substituted monomers and their respective polymers are made up of a related system of π electrons, that is, the electronic structures of the monomers and their corresponding polythiophene (and polypyrrole) must be alike [31]. This is not unreasonable since polythiophene (and polypyrrole) consists primarily of α,α'-linked monomer units [10,11]. The poly(2,5-thiophenediyl) structure is also produced by chemical synthesis [35] starting from 2,5-dibromothiophene.

With regards to the nature of the anion in the polythiophene films, the anion seems to influence the level of oxidation of the polymer. With the perchlorate and sulfate anions, the polymer oxidation level, about 0.1 [36], is twice as high as with the perfluoroborate and perfluorophosphate anions, 0.05-0.06 [6]. In addition, Hotta et al [36] recently reported that with certain anions the temperature used for the film preparation affects the properties of the film. For example, with sulfate anion, films prepared at 5°C are 10^3-10^4 times more conducting than those prepared at room temperature.

In considering substituent effects, we see in Table 9 that poly(3-methylthiophene) has a lower peak oxidation potential and a higher electrical conductivity [6] than the parent polythiophene. From the data of Tourillon and Garnier [37,38], we see that the conductivity of polythiophene increases

FIGURE 6 Peak oxidation potential of thiophene monomers versus their respective polymers in 0.1 M TBAFB·CH$_3$CN. (From Ref. 33.)

gradually with the incorporation of one and two methyl groups. This change in the electrical conductivity of the polymer which results from the introduction of methyl groups is not paralleled in the analogous pyrrole system. Table 6 reveals that the methyl-substituted polypyrroles have lower conductivities than the parent polypyrrole [6,25]. Apparently there is a delicate balance between electronic and steric effects, which can render substituted polymers of the five-membered heterocycles either more or less conducting than their parents.

A. Electroactivity

The details of the electroactive properties of these films have been previously considered [31,33,38] and no reiteration is necessary here. However, it is important to point out that these films can be cycled repeatedly between the oxidized conducting state and the neutral nonconducting state, an event which is accompanied by a reversible color change from green-black to pale copper, respectively. The cycling behavior is observed for polythiophene films derived from either the monomer or the 2,2'-dimer. The anodic peaks obtained from the dimer-derived polymer films, however, are noticeably sharper, with peak widths at half-height of about 90 mV for 60-nm films, while monomer derived films of the same thickness have a peak width at half-height of about 300-350 mV. Since it is known that the oxidation and reduction reaction is controlled by the diffusion of counteranions into and out of the surface-localized films [19,28], diffusion of ions through the dimer-derived film may be less limiting. This may also reflect the more regularly α,α'-linked monomer units in the dimer-derived film. The sensitivity of the electrical properties of polythiophene to linkages between monomer units other than α,α' bonds has been

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TABLE 9 Electrochemical Data for Some Conducting Polythiophene Films.

Polymerised monomer	Anion	$(\Omega^{-1}\ cm^{-1})$	Oxidation level	Reference
Thiophene	BF_4^-	0.02	0.06	6
"	BF_4^-	0.1	0.05	36
"	BF_4^-	10-20	0.3	37
"	PF_6^-	0.02	0.06	6
"	ClO_4^-	0.3	0.13	36
"	ClO_4^-	10-20	0.3	37
"	SO_4^{2-}	10^{-4}	0.1	36
"	$TCNQ^-$	10^{-4}	0.02	36
"	$CF_3SO_3^-$	10-20	0.3	37
Bithiophene	SO_4^{2-}	0.1	0.22	6
3-Methylthiophene	PF_6^-	1	0.12	6
"	ClO_4^-	10-30	0.25	37
"	$CF_3SO_3^-$	30-100	0.30	37
3,4-Dimethylthiophene	$CF_3SO_3^-$	10-50	0.3	37

pointed out by Sanechika et al [39]. In particular, they found that the electrical conductivity of polythiophene decreased with increasing β linkages introduced between monomer units.

The peak oxidation potential of polythiophene occurs at +1.0 V. This is far anodic of the peak oxidation potential of polypyrrole (-0.15 V), with the important consequence that polythiophene films are much more stable, especially to the presence of oxygen. Thus, unlike polypyrrole, neutral or electrochemically oxidized polythiophene films can be exposed to air, and even passed under a stream of oxygen, yet, when put back into an electrolyte solution and cycled electrochemically, they retain their switching capabilities. However, ESCA studies of the neutral films do reveal the presence of bonded oxygen at the surface of these materials. For neutral polythiophene films exposed to air for 24 hr, the C:S:O ration of 4.0:0.55:1.0, while a 14-day exposure reveals a C:S:O ratio of 4.0:0.5:1.0 [40]. However, the surface properties are not representative of the bulk properties of the films, as evidenced by its ability to retain electrochemical switching.

For successful performance of these materials in various applications such as in batteries, apart from the desirable electroactivity, the stability of the films under different conditions becomes of paramount importance. The oxidized conducting forms of the polythiophene films are remarkable stable under different conditions. For example, oxidized films placed in 6 M HCl or NaOH or in a solvent such as dichloromethane for 1 hr, do not

dissolve and they retain their electroactive properties when subsequently electrochemically cycled. The thicker films are also thermally stable to heating at 80°C for several hours. When kept for 3 hr at this temperature, polythiophene shows a decrease in conductivity from 0.1 to 0.04 $\Omega^{-1}\ cm^{-1}$, while heating for 20 hr results in a 10-fold decrease. Thin films which display a sensitivity of the switching behavior to changes in temperature between 0 to 80°C were found to be stable under these conditions for at least several hours. The electroactive properties were retained, and the peak oxidation potential shifted cathodically by 0.88 mV/deg with increasing temperature (Fig. 8). The shift in the oxidation potential was found to be reversible in this range. Finally, a noticeable sharpening of the anodic peak was observed at higher temperatures [33].

VIII. POLYSELENOPHENE

The propensity of the five-membered heterocyclic compounds, pyrrole, thiophene, and furan [32], to polymerize on anodic oxidation to produce highly conducting polymers ($10^{-5}<\sigma<10^2\ \Omega^{-1}\ cm^{-1}$) is not observed with selenophene [42]. Thus, when 10^{-3} M selenophene in 0.1 M electrolyte-acetonitrile solution is electro-oxidized (E_{pa}=1.86 V versus SSCE), a thin, nonconducting film is obtained. This surprising result may be due to steric effects. Droiding models of polyselenophene suggests a significant steric hindrance imparted by the relatively large selenium moiety, which should twist the linear polypyrrole-like polyselenophene chain. Although a conducting polymer need not have an absolutely planar backbone, planarity does affect conductivity [6]. A polymeric form of selenophene was obtained chemically, however, via cationic polymerization [41].
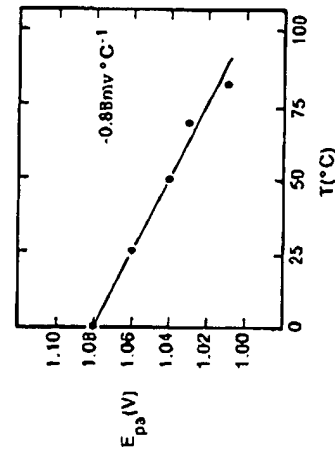
E_{pa} of polythiophene as function of temperature.

FIGURE 7 The shift in the peak oxidation potential of polythiophene as a function of temperature. (From Ref. 33.)

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IX. POLYAZULENE

Electrochemical oxidation of 10^{-3} mol/liter of azulene in acetonitrile containing 0.1 mol/liter of an appropriate electrolyte yields thick, amorphous, electrically conducting films [6,43]. These can be peeled off the Pt anode to provide free-standing, flexible films with electrical conductivities $10^{-2} < \sigma < 1 \ \Omega^{-1} \text{cm}^{-1}$.

Elemental analysis of these films is consistent for a polymer containing bis-coupled azulene units. The film also contains the anion of the electrolyte at typical concentrations of 1 per about 4 units of azulene. This situation closely resembles polypyrrole. The electrical conductivities of the polyazulene films depend upon the nature of the counteranion (Table 10), with perchlorate and tetrafluoroborate giving the highest values out of the selections investigated so far.

The n value for the film-forming reaction is 2.3, indicating that the poly-merization of azulene involves two electrons per monomer. The 0.3 excess charge required for the partial oxidation of the film is balanced by uptake of counteranions from the electrolyte. Thus the reaction for the preparation polyazulene shows electrochemical stoichiometry like polypyrrole.

A. Substituent Effects

For pyrrole, it is known that blockage of the α-positions, namely, the sites where linkage between the pyrrole units occurs in the polymer, will suppress polymerization [10,11]. Table 11 reveals that any 1-substituted azulene also fails to electropolymerize [6,43]. Accordingly, both the 1- and 3-positions of azulene have to remain unblocked to allow polymerization. However, 4,6,8-trimethylazulene, in which three positions of the seven-membered ring are simultaneously substituted, does yield a polymer, albeit of lower conductivity. These substituent effects suggest that the structure of polyazulene is best represented as poly(1,3-azulenediyl) (Fig. 8).

B. Mechanistic Considerations

The finding that the azulene units are connected exclusively via postions of the five-membered ring has the following implications for the reaction mecha-nism (Scheme 2). The originally formed radical cation in principle has two likely options: (a) It could react as an electrophile and attack neutral azulene

TABLE 10 Electrical Conductivity of Polyazulene Films

Counteranion	σ_{300} K $(\Omega^{-1} \text{cm}^{-1})$
BF_4^-	0.02-1
ClO_4^-	0.05
PF_6^-	0.03
$CH_3C_6H_4SO_3^-$	0.01

Source: Ref. 6.

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TABLE 11 Cyclic Voltammetric Data of Azulenes in 0.1 M TEAFB·CH3CN Versus SSCE

Compound	E_{pa} monomer	Produces polymeric film
Azulene	0.91	+
4,6,8-Trimethylazulene	0.90	+
1-Methylazulene	0.90	+
1-Phenylazulene	0.90	-
4,6,8-Trimethylazulene-1-aldehyde	0.89	-
Guaiazulene	0.71	-
1-(Phenylacetyleneny)azulene	0.90	-
1,3-Di(trimethylsilylacetyleny)azulene	1.04	-

Source: Ref. 6.

or (b) it could act as a radical and dimerize (i.e., combine with a second rad-ical cation). The hypothetical structure expected for the polymer would be different and thus depend upon the type of the polymerization mechanism. Thus electrophilic attack should cause a linkage between the position of the lowest π-electron density in the *radical cation* (i.e., the 4,6- or 8-position of the seven-membered ring [44]) and the site of *highest* π-electron density in neutral azulene (i.e., the 1- or 3-position of the five membered ring [44]). Accordingly, electrophilic addition of azulene radical cations to neutral azulene should result in poly(1,4-azulenediyl), which is not found, however. The conclusions drawn from substituent effects, namely, that polyazulene has a poly(1,3-azulenediyl) structure, therefore support the radical cation dimeriza-tion concept. This should lead to linkages between the 1-positions of the five-membered rings, namely, the position of highest spin density in the azulene radical cation [44], and the corresponding 1'-position of the other radical cation. Subsequent proton loss of the so-formed dication of the hydro-dimer would lead to the 1,1'-diazulene. Upon reoxidation, the radical cation
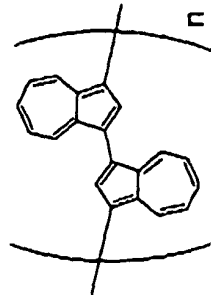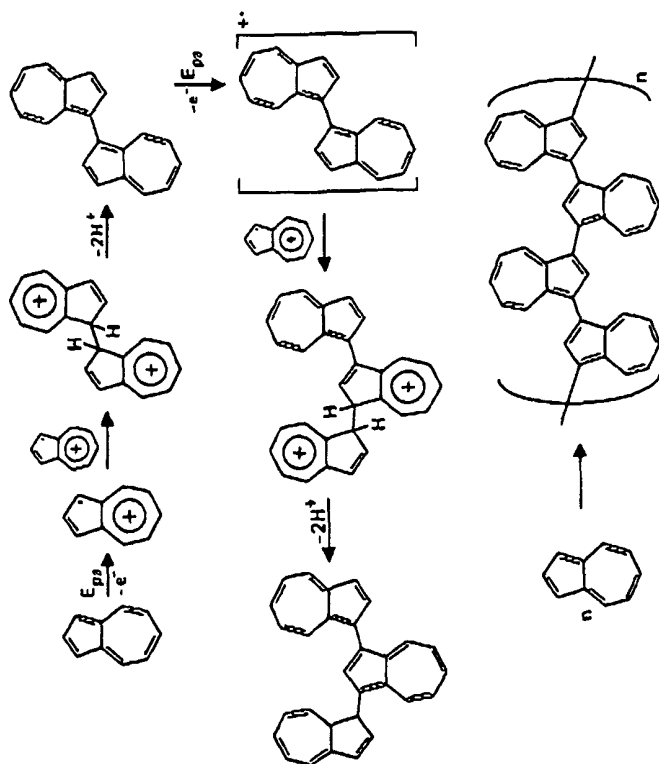

FIGURE 8 Proposed structure of polyazulene. (From Ref. 6.)

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of "impurities" is also known to govern synthesis of radical cation salts [45] which are alternate reaction products to the polymers discussed here.

The oxidation potential of the dimer IV is lower (0.6 V versus SSCE) than that of azulene. This is a characteristic feature of many families of homologous oligomers of aromatic compounds [18]. With regards to the follow-up reaction of the dimer cation, the most likely reaction pathway must involve reaction between the radical cations to produce the next higher dihydro-oligomer dications. Proton loss and subsequent reoxidation thus account for the polymerization reaction, which is essentially a cascade of electron transfer reactions (E) and chemical steps (C) for which, in extension of customary electrochemical abbreviation [46], the symbolism $E(CE)_n$ is suggested. Oxidation of the polymer and incorporation of counteranions leads to polyazulene films, as outlines in Scheme 2.

X. POLYCARBAZOLE

Electrochemical oxidation of 10^{-3} M carbazole in acetonitrile containing 10^{-1} M tetra-n-butylammonium perchlorate at +1.3 V versus SSCE yields an amorphous conducting film which adheres to the Pt anode [6]. Unlike polypyrrole, polythiophene, or polyazulene, these films are very brittle and crack easily. The films have low electrical conductivities of $10^{-4} < \sigma < 10^{-1}\ \Omega^{-1}\ cm^{-1}$ at 300°K, and the elemental analysis data, $(C_{12}H_{13}N)(ClO_4)0.45$, reveal that they are very rich in hydrogen and contain a high level of perchlorate anions. The films are most likely a mixture of low molecular weight oligomers, but certainly different from the crystalline radical cation salts obtained by Chiang et al, in very pure tetrahydrofuran as the solvent [45a]. The formation of film deposits on the electrode during oxidation of carbazole had previously been observed by Ambrose and co-workers, who had considered these films to be insulators [47].

The carbazole system, though yielding a very poor polymer or even only oligomers, is of interest from a reaction mechanistic point of view however. Chemical oxidation studies had shown already [48] that the chief oxidation products are four isomeric dicarbazyls and a small amount of trimer [49]. According to Maitland and Tucker [48], the reaction medium affects the isomer distribution drastically: In the presence of sulfuric acid, using dichromate as the oxidant, only the 3,3'-dicarbazyl is obtained, whereas in the absence of sulfuric acid, only the 3,3'-dicarbazyl is also formed. Electrochemical oxidation studies of Ambrose et al [47] revealed that the 3,3'-dicarbazyl is typically the dominating electro-oxidation product by far. The 9,9'-dimer was only formed very early during electrolysis, before the proton concentration buildup. Addition of H_2SO_4 suppressed the formation of the 9,9'-dimer altogether, whereas addition of base as a proton scavenger (pyridine) increased its yield significantly. These same authors showed further [47] that the 3,3'-dimer has a lower oxidation potential than the parent carbazole and the 9,9'-dimer a higher one instead.

For polymer formation, subsequent reoxidation of the dimer is essential. The 9,9'-dimer does not meet this requirement owing to its high oxidation potential; therefore, it would not propagate any further polymerization.

SCHEME 2 Electropolymerization of azulene. (From Ref. 6.)

of the dimer should show the same pattern of spin density distribution as the azulene radical cation. This means that the highest π-electron density in the radical cation of the dimer is expected to occur in the 3- (or 3'-) position. This site should therefore combine with the 1-position of the azulene radical cation to result in dihydrotrimer. Proton loss, reoxidation, and an extension of the above concept should lead to poly(1,3-azulenediyl), in agreement with the findings derived from the substituent effects.

At the anode surface radical cation dimerization is indeed a likely process. There the radical cation concentration is high, whereas the concentration of neutral azulene is low, minimizing the importance of any reactions involving neutral species. Thus the situation encountered here is very different from typical polymerization reactions occurring in the bulk, since there the concentration of neutral monomers is always much higher than those of the reactive intermediates.

The initial dimerization product of two radical cations is the dication of the dihydrodimer (III). The formation of this product is quite likely a reversible step, which becomes irreversible if subsequently two protons are removed, yielding the 1,1'-diazulyl (IV). Consequently, the radical cation combination will be very sensitive to the presence of proton acceptors even in trace amounts, such as bases, nucleophiles, or water. Sensitivity to trace amounts

TABLE 12 Properties of Polymeric Perchlorates Derived from Aromatic Monomers

Monomer		Polymer			
Compound	E_{pa} (V) monomer	E_{pa} (V) polymer	Elemental composition	Conductivity σ_{300K} (Ω^{-1} cm^{-1})	Density (flotation) (g/cm^3)
Azulene ($C_{10}H_8$)	+0.91	+0.65-0.70	($C_{10}H_{6.5}$)(ClO$_4$)$_{0.25}$	$1-2^{-1}$	1.35
Pyrene ($C_{16}H_{10}$)	+1.23	+1.1	($C_{16}H_{12}$)(ClO$_4$)$_{0.31}$	$10^{-1}$$_8$	1.34
Carbazole ($C_{12}H_9N$)	+1.30	+0.95	($C_{12}H_{13}H_1$)(ClO$_4$)$_{0.45}$	10^{-34}	1.36

Consequently, the polycarbazole-forming reaction must proceed via coupling in the 3-position to produce the poly(3,6-carbazolediyl) structure. Previous chronoamperometric and chronopotentiometric oxidation studies have shown that the n values of the carbazole oxidation reaction fall in the range 2.5-2.8. N-Alkyl-substituted carbazole, upon electro-oxidation, typically do not proceed beyond the dimer state [47].

XI. POLYINDOLE

Indole and its substituted derivatives undergo irreversible electro-oxidation. Thin films can be obtained from many substituted monomers, but most of these films passivate the electrode. Thicker films can be grown from indole, 5-cyanoindole, and 5-indolecarboxylic acid, for example. These films are very brittle and crack easily when removed from the electroplating solution [50]. Pressed films are conducting in the range $\sigma = 10^{-2}$-10^{-3} Ω^{-1} cm^{-1}. The structure of these polymers is currently unknown [32,50,51].

XII. POLYPYRENE AND POLYTRIPHENYLENE

In their earlier electro-oxidation studies of a variety of polyaromatic hydrocarbons, Peover and White [52] had already found that pyrene and triphenylene caused deposition of insoluble films on the electrode, which they had considered to be insulating. More recently, [6] it has been demonstrated, however, that these deposits are conducting, and the conductivity of polypyrene-ClO$_4$ after peeling it off the anode is 10^{-1}<σ<1 Ω^{-1} cm^{-1}. Table 12 lists the electrochemical and elemental analysis data for polypyrene in comparison with polyazulene and polycarbazole. Their structures are unknown at present, but can be assumed, based on the concept of radical cation dimerisation developed above. Polypyrene, for example, is expected to be made up of 1,6-pyrenediyl and/or 1,8-pyrenediyl units. These structures are shown in Scheme 3 along with the mechanism of the formation.

XIII. POLYANILINE

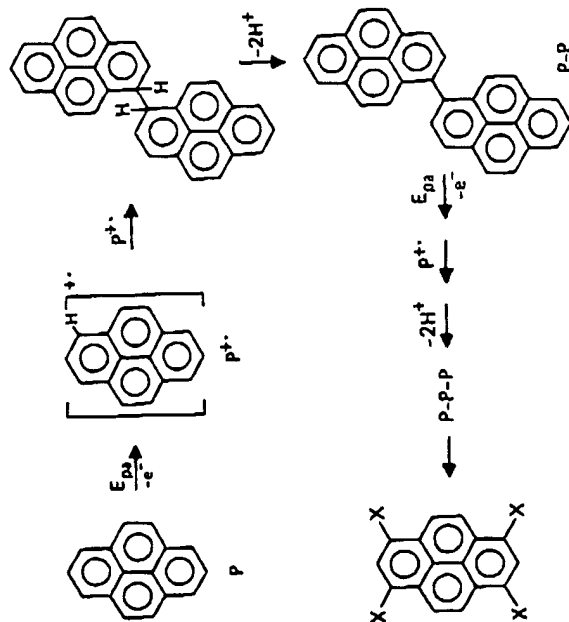The electropolymerization of aniline to produce aniline black was first reported 20 years ago [53,54]. The material was pepared by the electro-oxidation of aniline in aqueous H$_2$SO$_4$ solution using a constant anodic potential. The reaction is described as a bimolecular reaction involving a radical cation intermediate. The reaction has a ΔH equal to 121 kJ/mol and an an value equal to 1.2-1.3 [53], where n=2. The reaction produces benzidine and 4-aminodiphenylamine as soluble by-products to the aniline black product. Aniline black is described as a dark, amorphous material whose color can vary from dark green to blue-violet. It is structurally similar to the aniline octamers emeraldine and nigraniline. The polymer consists of aniline units which are para-coupled, with both head-to-tail and head-to-head linkages being formed [54].

In our laboratory [55] we found that the electro-oxidation of aniline at constant potential produces a powder which adheres poorly to the electrode.

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SCHEME 3 Electropolymerization of pyrene. (From Ref. 6.)

On the other hand, electro-oxidation of aniline by continuously cycling the potential between -0.2 and +0.8 V (versus SSCE) produces an even film which adheres strongly to the electrode surface. These films are electroactive and the oxidation reaction is chemically reversible. As can be seen in Figure 9, the reaction is very complicated, where several peaks appear in the region between -0.2 and +0.4 V. The oxidation of the polymer is not a simple electron transfer and must be accompanied by a series of deprotonation reactions to produce quinoidal structures along the polymer chain. This is shown schematically in Eq. (4):
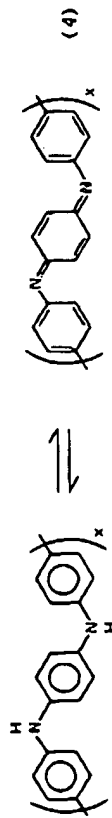
XIV. POLYPHENYLENE

The simplest of the aromatic compounds, benzene, has also been electropolymerised to produce films on electrode surfaces. Because of the high potentials required to oxidize benzene in the conventional electrolytic solutions, these reactions have been carried out in strong acid media, such as, HF [56, 57], liquid SO_2 [58], HCl-AlCl$_3$ [59], and HF-SbF$_5$ [60]. These preparations are performed in polyethylene or polypropylene cells using a platinum, gold,
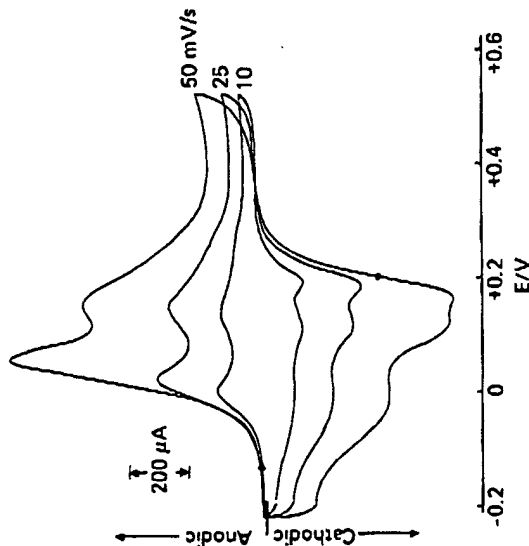
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FIGURE 9 Cyclic voltammogram of a polyaniline film on a Pt electrode in aqueous 0.1 M H_2SO_4 solution using an SSCE reference electrode. (From Ref. 55.)

or glassy carbon working electrode and a polymer-coated Ag-AgCl [60] or Pd-H$_2$ [57] reference electrode. The resulting films are amorphous and poorly conducting [60] and consist of o- and p-coupled phenylene units [56]. It was recently reported [57] that electroactive films could be prepared in a 93% HF-benzene two-phase system by sweeping the voltage continuously between 0 and 1.2 V. The initial scan shows only a sharp rise in current at about +1.1 V and, as characteristic for all the aromatic compounds considered in this report, polymerization occurs only when the voltage scan extends into this region. The resulting film switches at 0.4-0.6 V in this electrolyte solution. As with polypyrrole, the film can be further modified by nitration and sulfonation [57].

XV. CHEMICALLY PREPARED POLYAROMATIC POLYMERS

Linear polyaromatic polymers have been of interest to organic chemists, and the preparative routes to these compounds were available long before we reported the electrochemical routes to these polymers. The strongest efforts in this field have been in the laboratories of Kovacic and Yamamoto. Poly-p-phenylene has been synthesized by coupling benzene with an aluminum chloride-copper chloride catalyst [61,62] and by coupling the grignard reagent of p-dibromobenzene [63]. The resulting polymer can be oxidized with arsenic pentafluoride and has conductivities of about $0.01\ \Omega^{-1}\,\mathrm{cm}^{-1}$. Poly(2,5-thiophene) [35,64] and poly(2,4-thiophene) [65] were prepared by coupling

the Grignard reagent of the corresponding dibromethiophene using nickel chloride-bipyridy [35] or nickel acetoacetate to promote the reaction [64]. The oxidized form of the poly(2,5-thiophene) polymers has conductivities of $0.1 \, \Omega^{-1} \, cm^{-1}$, while the poly(2,4-thiophene) polymers show only a small change in conductivity when treated with an oxidizing agent. Copolymers of thiophene containing 2,5- and 2,4-substituted rings have also been prepared [39]. The effect of incorporating the 2,4-thiophene unit is to drastically reduce the conductivity of the oxidized polymer. Poly(2,5-selenophene) was also prepared by coupling the Grignard reagent of 2,5-dibromoselenophene using nickel salts [66]. We have already mentioned that these polymers are easily oxidized with chemical oxidants, although the electroactive properties have not been determined.

Polymers of pyrrole derivatives have also been prepared by chemical routes. N-Substituted polypyrrole polymers were prepared where the substituent is methyl, benzyl, or phenyl [67,68]. In each case the polymer was synthesized by coupling the Grignard reagent of the corresponding N-substituted 2,5-dibromopyrrole derivative. The resulting polymers were oxidized with iodine or arsenic pentafluoride. In the case of poly-N-methylpyrrole, the conductivity of the oxidized polymer was similar to that for the electrochemically prepared polymer. The polymers with the aryl substituents had very low conductivities. In contrast with the polymers which are prepared electrochemically, these polymers are moldable and solution processible [67, 88]. In a separate study thin films of polypyrrole were grown on the meniscus of an aqueous alcohol solution containing 1.2 M sulfuric acid [69]. The films could be oxidized with bromine and iodine vapors to produce dark brown films which were marginally conducting. The oxidized form of these films were not stable in air.

Wellinghoff et al. [70] recently reported the preparation of linear polymeric products via chemical polymerization starting from N-methyl-3,6-dibromocarbazole. These chain molecules dissolve in nitrobenzene, can be cast into a film, and turn conducting upon doping with $I_2 \cdot Br_2$. The electrical conductivities of the air-stable, black, doped films are around $1 \, \Omega^{-1} \, cm^{-1}$. Their structure follows readily from the synthetic concept as poly(N-methyl-3,6-carbazolediyl), in agreement with the considerations outlined above for polycarbazole. High molecular weight chains of the parent polycarbazole should be accessible in a similar fashion.

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